7

MOLECULAR ORBITAL THEORY OF THE LIGAND FIELD IN TETRAHEDRALLY CO-ORDINATED Ni^{2+} COMPLEXES

R. RAI AND S. MITRA

MAGNETISM DEPARTMENT,
INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE
JADAVPUR, CALCUTTA-32.

(*Received, January 25, 1964*)

A strong cubic ligand field splits the $3d^8\ ^3F$ ground state of Ni^{2+} into three levels $^3T_1$, $^3T_2$ and $^3A_2$ with separations of the order of 10^4 cm^{-1}. In tetrahedrally co-ordinated Ni^{2+} complexes, the cubic field coefficient is $-4,9$ that of the octahedrally co-ordinated ones, so that (1) in the former the orbital triplets $^3T_1$ lies lowest while in the latter it is the orbital singlet $^3A_2$; also (2) the corresponding cubic separa- tions in the former are less than half of those of the latter (Van Vleck, 1932; Gorter, 1932, Bleaney and Stevens, 1953).

A Ni^{2+} ion can be treated as a system consisting of two d-holes in which the three lowest states $^3T_1(F)$, , $^3T_2(F)$ and $^3A_2(F)$ arise out of $(t_{2g})^2$, $(t_{2g})^1(e_g)^1$ and $(e_g)^2$ configurations respectively, so that the determinantal wavefunctions of the lowest triplet $^3T_1(F)$ is

$$\begin{aligned} \psi_1 &= |\ t_c\ t_a\ | \\ \psi_2 &= |\ t_a\ t_b\ | \\ \psi_3 &= |\ t_b\ t_c\ | \end{aligned} \qquad \ldots\ (1)$$

where t_a, t_b, t_c etc are single d-electron or hole orbitals in t_{2g} configuration, inclusive of the admixtures of excited $3d^74p$ confiiguration orbitals (coming due to the absence of centre of inversion in the tetrahedral complexes) and of ligand s- and p-orbitals. Thus following Bates and others (Bates, 1962, Bates *et al*, 1962) and Wholfsberg and Helmotz (1952)

$$t_a = |xy\rangle = N\ \frac{1}{(1+\gamma^2)^{\frac{1}{2}}}\ \{dxy+\gamma\,|z\rangle\}+\frac{\lambda}{2\sqrt{2}}\Big\{(\sigma_1+\sigma_4\qquad -\sigma_3)$$

$$+\tfrac{1}{2}\ (\pi_{x3}+\pi x_2-\pi x_1-\pi x_4)+\frac{\sqrt{3}}{4}\ (\pi y_4+\pi y_1-\pi y_2-\pi y_3)\Big\}\Big]$$

$$= |yz\rangle = \mathrm{N}\ \Big[\ \frac{1}{(1+\gamma^2)^{\frac{1}{2}}}\ \{dyz+\gamma\,|x\rangle\}+\frac{\lambda}{2\sqrt{2}}\Big\{\ (\sigma_1+\sigma_3-\sigma_2-\sigma_4)$$

$$+\tfrac{1}{2}(\pi x_4+\pi x_2-\pi x_1-\pi x_3)+\frac{\sqrt{3}}{2}(\pi x_4+\pi y_2-\pi x_1-\pi y_3)\Big\}\Big]$$

$$t_c = |xz> = N\Big[\frac{1}{(1+\gamma^2)^{\frac{1}{2}}}\{dxz+\gamma|y>\}+\frac{\lambda}{2\sqrt{2}}(\sigma_1+\sigma_2-\sigma_3-\sigma_4)$$

$$+(\pi x_1+\pi x_2-\pi x_3-\pi x_4)\Big\}\Big]$$

where N is the normalizing factor; λ is a measure of amount of admixture of the ligand s- and p-orbitals with the central $3d^8$ orbitals; dxy etc represent the large $3d$ contributions and $\gamma|z>$ etc. the $3d^8\ 4p$ contributions. Now if we choose trigonal axis as the axis of quantization, the appropriate orbital states for the lowest triplet is

$$|+> = -\frac{1}{\sqrt{3}}[\omega|\psi_1> +\omega^2|\psi_2> +|\psi_3>]$$

$$|0> = \frac{1}{\sqrt{3}}[|\psi_1> +|\psi_2> +|\psi_3>] \qquad \ldots (3)$$

$$|-> = \frac{1}{\sqrt{3}}[\omega^2|\psi_1> +\omega|\psi_2> +|\psi_3>]$$

where $$\omega = \exp\left(\frac{2\pi i}{3}\right)$$

and the appropriate Hamiltonian is

$$\boldsymbol{H} = V_{trig}+\alpha u_\zeta s_\zeta+\alpha'(u_\xi s_\xi+u_\eta s_\eta) \qquad \ldots (4)$$

where α and α are the effective orbital Lande g-factors (Abragram *et al*, 1951) parallel and perpendicular to the trigonal axis and takes into account the effect of upper $^3T_1(P)$, $^3T_2(F)$ and $^3A_2(F)$ with the lowest triplet $^3T_1(F)$. Operating upon wavefunctions (3) by above Hamiltonian and solving the secular determinant we get the resulting energies and wavefunctions, over which the magnetic perturbation $H_1 = \beta H(L+2s)$ can be applied. Thus solving in detail the first order and second order magnetic perturbations as usual we have deduced an expression for the mean susceptibility for trigonally distorted Ni^{2+} tetrahedral complexes and have compared with experimental measurements on $[Et_4N]_2[NiBr_4]$. It may be mentioned here that $[Et_4N]_2[NiBr_4]$ is a cubic crystal (space group P_{21}, with four ions in the unit cell, $a = 15°.5$Å) and has a trigonal distortion of the

halogen tetrahedron round the Ni^{2+} ion, the trigonal axis passing through one halogen at the vertex of the tetrahedron and the Ni^{2+} ion and normal to the base formed by the other three equivalent halogens. (X-ray studies of Peter Pauling-reference by Gill *et al*, 1959)

TABLE.

Temp °k	A_2 cm^{-1}	A_4 cm^{-1}	Δ cm^{-1}			$k \times 10^6$ (Theo)	$k \times 10^6$ (Exp.)
300	291	80	− 780	0.94	1.67	5995	5986
260	282	88	− 900	0.90	1.69	6828	6840
180	265	95	−1020	0.876	1.71	9520	9536
140	254	102	−1096	0.84	1.73	11900	11909
100	245	110	−1110	0.761	1.76	15980	16000

From the above table we see that the agreement between the theoretical and experimental results is good, provided the second and fourth order trigonal field parameters A_2 and A_4 be allowed to change from 291 cm^{-1} and 80 cm^{-1} at room temperature to 245 cm^{-1} and 110 cm^{-1} at 100°K. These in turn change the trigonal separation Δ from −780 cm^{-1} to −1110 cm^{-1}, α from .94 to .761 and α' from 1.67 to 1.76. The values of the other parameters used are

$$Dq = 380\ cm^{-1}, \qquad \zeta_{\|} = -274\ cm^{-1} \qquad \zeta_{\perp} = -217\ cm^{-1}$$

$$k_{\|} = .95 \qquad k_{\perp} = .80$$

where $\zeta_{\|}$ and $\zeta_{\perp}$ are the effective spin-orbit coupling coefficients inclusive of the effects of $3d^8$ and $3d^74p$ configurational interaction and convalency overlap between the central orbitals of Ni^{2+} ion and s and p orbitals of the ligand atoms. $k_{\|}$ and $k_{\perp}$ are the effective orbital reduction factors inclusive of the same interactions as above.

Details of the theoretical and experimental results will be published shortly elsewhere.

ACKNOWLEDGMENT

The authors express their deep sense of gratitude to Prof. A. Bose, D.Sc., F.N.I. for his guidance and valuable suggestions.

REFERENCES

Abragam, A. and Pryce M. H. L. 1951, *Proc. Roy. Soc.* **A206**, 173.

Bleany, B. and Stevens K. W. H. 1953, Reports on Prog. *Phys.* **16**, 108.

Bates, C. A. 1962, *Proc. Phy. Soc.* **78**, 69.

Bates, C. A. Moore, W. S. Standley, K. J. and Stevens, K. W. H. 1962, *Proc. Phys. Soc.* **69**, 73.

Gill M. S. and Nyholm R. S, 1959, *Jr. Chem. Soc.* 3997.

Gorter, C. J. 1932, *Phys. Rev.* **42**, 427.

Van Vleck J. H. 1932, *Phy. Rev.* **41**, 208.

Wolfsberg, M. and Helm hol , L., 1952, *J. Chem. Phys.*, **20**, 837.